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Wetting of Decagonal $Al_{13}Co_4$ and Cubic AlCo Thin Films by Liquid Pb

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ABSTRACT

Wetting of µm-sized Pb droplets on thin polycrystalline films of decagonal $Al_{13}Co_4$ and cubic crystalline AlCo phases is reported. The sample preparation is crucial to have Pb droplets lying on a clean surface. Decagonal and cubic films were prepared under high vacuum conditions, by sequential deposition and annealing of specific stackings of Al and Co layers of nanometric thicknesses. A 300nm-thick Pb slab was then deposited on the top of the films. Dewetting experiments were performed in situ in a scanning Auger microprobe where the surface chemistry can be monitored: the Pb slab dewetts into droplets. The wetting of Pb on both substrates was found to be similar with contact angles around 45°.

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Keywords: wetting; scanning Auger microscopy; intermetallic, cubic AlCo; decagonal $Al_{13}Co_4$;

1. INTRODUCTION

Quasicrystals (QCs) were discovered over 20 years ago [1]. Their bulk atomic structures can be described as a relatively compact quasiperiodic stacking of atoms or clusters of atoms in which typical structural defects develop. QC display bulk physical properties, like low thermal and electrical conductivity that are specific to their structure. Moreover, unusual surface properties have been reported, including low friction coefficients, high contact angles with water and good resistance to oxidation [2, 3]. Because these anomalous surface properties were investigated in air, an environment where aluminium-rich materials are covered with an aluminium oxide layer, it may be debated wether the observed surface properties are due to the oxide layer, or specific to the quasicrystalline structure.

The first studies of clean surfaces of quasicrystals were published in the early 1990's (for a review see [4]). They were focusing on the atomic and electronic structures of the surface. In order to get rid of the oxide layer, several methods have been proposed (cleavage, sputtering, annealing,…) [5]. However they alter the quasicrystallinity of the surface or are not suitable for carrying out wetting experiments.

The present study describes the wetting of Pb, a metal with a low melting point, on the surfaces of two compounds made of the same components, Al and Co, but with different crystal structures. They are the CsCl-type crystal, AlCo, and the decagonal phase $Al_{13}Co_4$. Special care has been taken to prevent the formation of an aluminium oxide layer on the surface of the Al-Co phases before, and during the wetting experiment. Thus, our method has allowed, for the first time, the study in clean conditions of the wetting of a liquid metal on crystalline and quasicrystalline surfaces.

2. EXPERIMENTAL

An suitable method for studying the wetting of oxidizable surfaces is the dewetting of thin (~100nm) slabs [6]. First, the films of Al-Co compounds are prepared (as explained below [7]) in an ultra high vacuum deposition chamber. Then, in the same apparatus and without breaking the vacuum, the lead slab is deposited on the Al-Co substrates. This constitutes the original feature of the process. In addition, the lead layer protects the quasicrystalline surface when the samples are transferred to the scanning Auger microprobe (SAM).

In a previous publication [7], we have shown that a stack of Al/Co bilayers of nanometric thickness forms, upon annealing at about 700K, a single-phase decagonal quasicrystalline film with homogeneous microstructure. The multilayers (300nm) were made by successive electron-beam evaporation of high-purity Al (99.9999 at.%) and Co (99.9999 at.%) on an oxidized Si substrate at room temperature. The base pressure during the evaporation was in the 10^{-4}-10^{-5} Pa range for both metals. The Al and Co layer thicknesses were monitored during evaporation with a quartz balance. The nominal [Al]/[Co] atomic ratio of the sample corresponds to 13/4 or 1/1, respectively. The transformation into $Al_{13}Co_4$ and AlCo was achieved by an appropriate annealing treatment [7].

After preparation, the Al-Co/Pb sample was transferred *in* air, from the deposition chamber to a CAMECA Nanoscan 100 scanning Auger microprobe, equipped with a STAIB Instruments analyzer, a 6 keV CAMECA Duoplasmatron ion gun, and a home-built heating unit. Both surface composition analysis and imaging of the particles were undertaken within the SAM. This facility is located at the CRMC-N.

The base pressure in the SAM chamber was $1 \cdot 10^{-8}$Pa. The surface of the Pb film was first cleaned by ion bombardment, to remove surface contamination gathered during sample transfer. Then the sample was gradually heated, with periodic interruptions during which it was lightly sputtered so as to remove any impurities that may have segregated to the surface. The cleaning process was monitored by Auger electron spectroscopy (AES).

Upon heating above the melting point of Pb (600K), the lead film dewetted the substrate by forming droplets. The surface chemistry of the Al-Co films in-between the droplets was examined by AES. No carbon was detected but oxygen is present in small quantities at the surface of the Al-Co films. Fig.1 displays an Auger spectrum at high energy, in the derivative mode, where the Auger transition of aluminium appears as metallic. Thus we conclude that the oxygen detected at the surface of the Al-Co compounds is present as adsorbed species at the surface of the Al-Co compounds.

The Pb droplets display in the SAM contact angles lower than 90°. To optimize the wetting measurements, the droplets were frozen and the sample was transferred to a field emission gun scanning electron microscope where pictures of the droplets were obtained with a high resolution. Since there was no significant change of the shape of the droplets after solidification, the measured contact angles were taken as those of the frozen-in Pb droplets.

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3. RESULTS AND DISCUSSION

The figures 2 are general views of the two samples at low magnification. They display Pb droplets uniformly distributed on the samples. The contact circles have diameters of several µm. Figure 3 shows details of typical Pb droplets on which the contact angles are measured. The contact angles, averaged over several droplets, are 42±5° and 49±7° on AlCo and $Al_{13}Co_4$ respectively. This difference is not significant given experimental scatter.

The contact angle of a liquid on a homogeneous surface is given by the Young equation:

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \qquad (1)$$

where the γ_{ij} are the interface energy of the three interfaces (l = liquid, s = solid and v = vapor).

It should be emphasized that once the contact angle and the surface energy (surface tension) of the liquid are known, Eq. 1 only gives the difference between the solid/liquid and solid/vapor energies, but not the absolute value of the surface energy of the compound.

To our knowledge there are only estimates [9] but no data on the surface energies of intermetallic compounds. However, we can compare the wetting behaviour of Pb (20K above its melting point) on the Al-Co compounds with the behaviour of Pb on Al_2O_3 and on pure Al and Co.

The contact angles of Pb on alumina single-crystal and on thick native oxide of aluminium have been reported to be 127±3° and 130±5°, respectively [10]. They are much larger than 90°. Comparison of these contact angles with those measured for the two Al-Co compounds show clearly that the Pb droplets do not lie on aluminium oxide, as already suggested by the Auger spectrum of Fig. 1. On the other hand, contact angles of Pb on aluminium single crystal and on polycrystalline film of Al are close to 30±5° [10,11]. It is only on polycrystalline films of Co that the contact angle of Pb, 50±6° [12], is similar to that on AlCo and $Al_{13}Co_4$. Thus the wetting behaviour of Pb on both Al-Co compounds is closer to that on a surface of a metal of high melting point.

4. Summary

The aim of this study was to compare the wetting of a low melting point metal on two Al-Co compounds, one with a CsCl crystalline structure and the other with a quasicrystalline decagonal structure. A challenging point was to design a method where the liquid metal is put into contact with the aluminium-rich compound without need of removing any oxide from the substrate. This was done by preparing films of the compounds and by covering them with a thin Pb slab in a UHV chamber. The thinPb slab was subsequently dewetted to form droplets of micrometer size. The dewetting experiment was performed in a scanning Auger microprobe, in which the surface chemistry can be monitored.

The measured contact angle of liquid Pb (45°) on the Al-Co compounds, when compared to that previously obtained on thick native oxide of aluminium (130°), confirms that our experiments were carried out in clean conditions. Our main new result is that the contact angles observed on both Al-Co compounds are similar, wether their structure is decagonal or cubic. Both compounds are aluminium-rich, but they are not wet like a simple metal such aluminium. Further interpretation of our results requires a better description of the surface of these complex compounds.

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Deleted: In conclusion, as far as wetting is concerned, both Al-Co compounds behave like metallic compounds. However we emphasize that this result does not infer any conclusion about metallic character of the surface of the compounds.¶
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Figures captions

Fig.1 : Auger spectrum in the derivative mode, of the substrate $Al_{13}Co_4$ between Pb droplets taken after fragmentation of the Pb layer. It displays the KLL Auger transition of Al.

Fig.2 : Low magnification SEM images of the distribution of the Pb droplets lying on the AlCo and $Al_{13}Co_4$ substrates after freezing.

Fig.3 : High magnification SEM images of Pb droplets on the AlCo and $Al_{13}Co_4$ substrates after freezing. Several of such images were used to measure the contact angles.

Figure 1

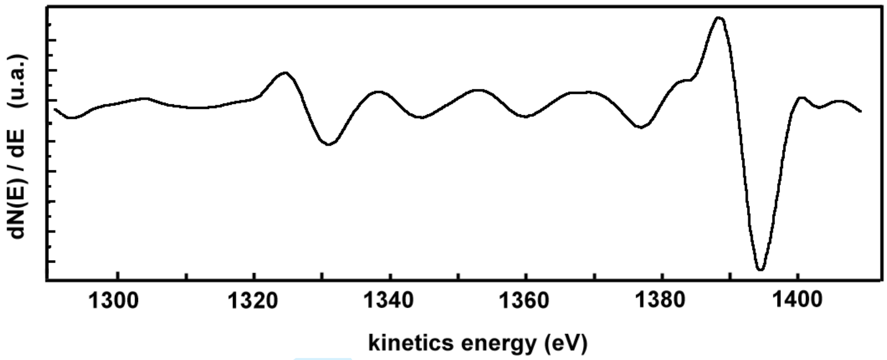
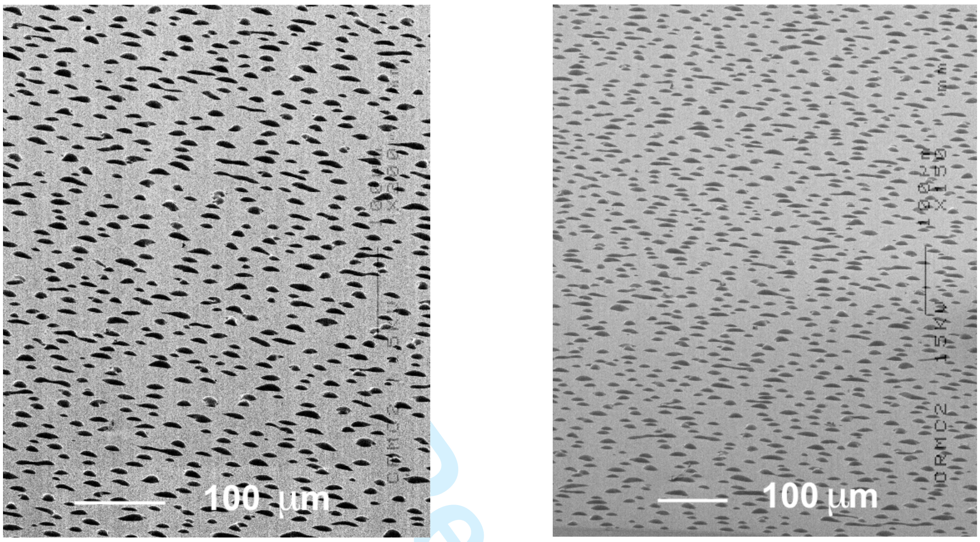
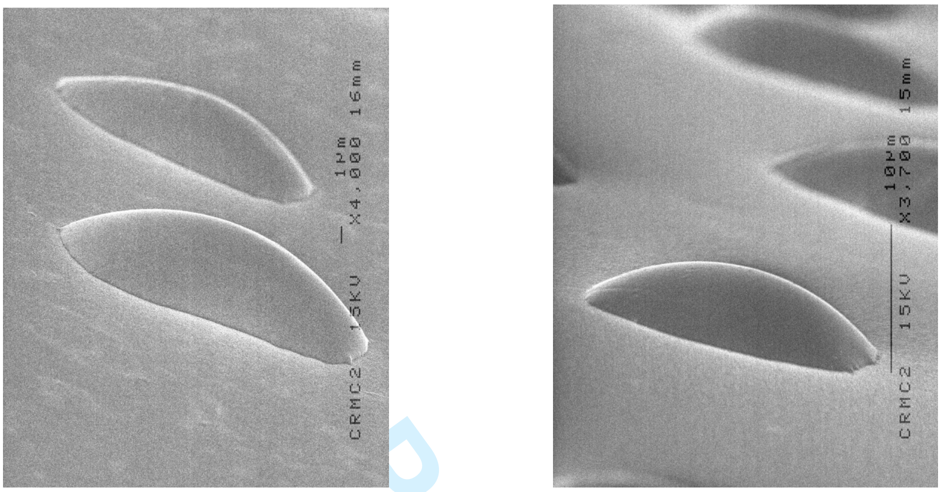


Figure 2



AlCo **$Al_{13}Co_4$**

Figure 3



AlCo **$Al_{13}Co_4$**